



(11) **EP 2 508 496 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**10.10.2012 Bulletin 2012/41**

(51) Int Cl.:  
**C04B 28/10 (2006.01) C04B 28/18 (2006.01)**

(21) Application number: **11002869.3**

(22) Date of filing: **06.04.2011**

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**

(71) Applicant: **HeidelbergCement AG**  
**69120 Heidelberg (DE)**

(72) Inventors:  
• **Bullerjahn, Frank**  
**69123 Heidelberg (DE)**  
• **Zajac, Maciej**  
**69126 Heidelberg (DE)**

(74) Representative: **Wagner, Jutta et al**  
**Patentanwälte**  
**Zellentin & Partner**  
**Rubensstrasse 30**  
**67061 Ludwigshafen (DE)**

(54) **Magnesia based binder composition**

(57) The present invention relates to a binder composition comprising magnesium oxide, a reactive  $\text{SiO}_2$  and a hydrated magnesium carbonate of formula  $x \text{MgCO}_3 \cdot y \text{Mg}(\text{OH})_2 \cdot z \text{H}_2\text{O}$ , wherein  $x \geq 1$ , the carbonate may be non-stoichiometric, and at least one of  $y$  or  $z \geq 0$  and  $x, y, z$  may be integers or rational numbers, wherein

the weight ratio of magnesia to hydromagnesite ranges from 1:20 to 20:1. The invention further relates to building materials made from the binder composition and to its use in construction.

**EP 2 508 496 A1**

## Description

**[0001]** The present invention relates to a binder composition based on magnesia, to building materials comprising it and to its use in construction.

**[0002]** Sorel cement (also known as magnesia cement) is a hydraulic cement first produced by Stanislas Sorel in 1867. The cement is a mixture of magnesium oxide (burnt magnesia) with magnesium chloride with the approximate chemical formula  $Mg_4Cl_2(OH)_6(H_2O)_8$ , corresponding to a weight ratio of 2.5-3.5 parts MgO to one part  $MgCl_2$ . In use it is typically combined with filler materials such as sand or crushed stone. It is used for grindstones, tiles, artificial stone (cast stone), cast floors, and even artificial ivory (e.g. for billiard-balls). It can withstand 10,000 - 12,000 psi of compressive force whereas standard Portland cement can only withstand 2,000 psi. Its chief drawback is its poor water resistance, making it unsuitable for construction applications. In addition, it is relatively expensive compared to standard concrete and gypsum.

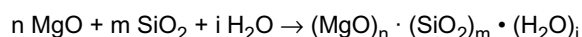
**[0003]** There have been numerous proposals for overcoming the problems outlined above. An overview can be found in WO 2009/156740, which itself proposes to use a mixture of magnesia and hydrated magnesium carbonate as binder composition.

**[0004]** However, there still remains a need for low energy and low carbonate emitting binders.

**[0005]** Surprisingly it has been found that a mixture of magnesia, hydrated magnesium carbonate and a reactive  $SiO_2$  provides a binder composition with more or less similar properties as portland cement, i.e. hardening or setting with water, respectively.

**[0006]** Thus, the present invention solves the object by providing a binder composition comprising magnesia, a reactive  $SiO_2$  and a hydrated magnesium carbonate of formula  $x MgCO_3 \cdot y Mg(OH)_2 \cdot z H_2O$ , wherein  $x \geq 1$  and at least one of  $y$  or  $z \geq 0$  and  $x, y, z$  may be integers or rational numbers, wherein the weight ratio of magnesia to hydrated magnesium carbonate ranges from 1:20 to 20:1. The invention further solves the problem with building materials made from the binder composition and its use in construction.

**[0007]** The early strength of this new binder comes from the formation of brucite, magnesium silicate hydrate (MSH) and possibly from amorphous hydrated magnesium carbonate. The novel binder is further hardening in contact with water due to the ongoing formation of amorphous and water insoluble magnesium silicate hydrate according to the general reaction equation



wherein  $n, m$  and  $i$  are all  $> 0$ , and can, independently from each other, be integers or rational numbers. Mg can be partially substituted by minor amounts of e.g. Ca, Na, K, Li, Ba, Al, Fe, Zn, Mn and / or trace elements like Cr, B, Co, Ni, Cu, As, Be, Rb, Sr, Cs, can be contained. The MSH gel can also contain minor amounts of  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $HS^-$ ,  $S^{2-}$ ,  $N^{3-}$ ,  $P^{3-}$ ,  $As^{3-}$ ,  $B^x$ , acetate, formate, citrate, oxalate, etc. The binder forms a body with high early compressive strength, a high ultimate strength, good stability below water and corrosion resistance against acid and alkaline solutions.

**[0008]** One advantage of the binder according to the invention is that the temperature needed for the calcination of  $MgCO_3$  (normally around  $750^\circ C$ ) is substantially lower than that for sintering the raw materials of portland cement. Thereby a considerable amount of  $CO_2$  can be avoided, i.e. carbonate emission of the binder be reduced, compared to portland cement based binders. Another advantage is the possibility of using natural magnesium silicates, like for example olivine, serpentine and talc, as raw materials providing an additional carbon dioxide reduction. The sources of magnesium silicates and carbonates are globally widespread and most often located close to the surface. They can be mined with state of the art technologies. Still another advantage is the possibility of using relatively high amounts of natural and/or artificial puzzolans, waste etc. as raw materials.

**[0009]** The first component of the binder according to the invention is magnesium oxide, MgO. Possible sources of magnesium oxide are natural magnesium carbonates or magnesium containing carbonates [e.g. Magnesite, magnesium rich limestone, Dolomite, etc.], magnesium (containing) hydroxides and silicates as well as synthetic magnesium sources. Magnesium oxide is usually prepared by calcination. Useful are magnesium oxides that are low burned, i.e. from  $400$  to  $<750^\circ C$ , middle burned, i.e. from  $750^\circ C$  to  $<1100^\circ C$ , and hard burned, i.e. at  $\geq 1100^\circ C$ , as well as mixtures of two or all of these. The amount of magnesium oxide in the material used should be at least 95 %. Especially the iron content should preferably be kept as low as possible, as iron induces a significant decrease of the compressive strength. The calcium content should preferably be below 2 %, because in contact with water and hydrated magnesium carbonate calcium induces a fast stiffening as a result of the precipitation of calcite.

**[0010]** To achieve a fast setting mainly or exclusively low burned magnesium oxide should be used. For other demands the low temperature calcined magnesium oxide content can decrease to 10 % while the content of middle and minor hard burned magnesium oxide increases.

**[0011]** The surface of the magnesium oxide depends on the method of manufacturing it, typically it has a surface of more than  $10 m^2/g$ , as measured according to the Brunauer-Emmett-Teller (BET) method. Particularly useful is soft

burned MgO with a surface of around 30 m<sup>2</sup>/g and of more than 60 m<sup>2</sup>/g.

**[0012]** The second component is a reactive silica, SiO<sub>2</sub>. The term reactive silica denotes both natural and artificial SiO<sub>2</sub> that is able to undergo a hydraulic setting/hardening in presence of a suitable reactant which is MgO according to the invention. One possibility to determine the amount of reactive silica in a material is measurement of the soluble SiO<sub>2</sub> according to DIN EN 196-2. Other methods may be used. With methods relying on dissolution of the silica it is important that for materials with high proportion of reactive silica the results are not influenced by saturation effects. A lot of substances can be used as source of reactive silica like diatomaceous earth, micro-silica, silica fume, fine to ultra-fine quartz powder, (calcined) siliceous earth, natural puzzolans, synthetic puzzolans, blast furnace slag, fly ash, burnt oil shale, sewage sludge ash, rice husk ash, glass powder, etc. The amount of reactive silica in the material used should be at least 10 %, preferably at least 30 %. A SiO<sub>2</sub> comprising material which does not contain reactive silica or only traces is not useful, e.g. siliceous sand. The reactive silica should preferably be in the form of amorphous SiO<sub>2</sub>. A material with a high proportion of reactive silica such as micro-silica and silica fume provides higher early strength and is preferred when such early strength is important. The material used as source of reactive silica typically has a Blaine surface of at least 2000 cm<sup>2</sup>/g, preferably from 2500 to 11000 cm<sup>2</sup>/g, most preferably from 3000 to 6000 cm<sup>2</sup>/g.

**[0013]** In one preferred embodiment it is possible to partially or wholly replace magnesium oxide and reactive silica as separate raw material components by natural or artificial magnesium silicates, preferably natural magnesium rich silicates. Depending on the composition of the magnesium silicates either magnesium oxide or a source of reactive silica can be added. These materials should be pretreated to destroy the crystal lattice of the minerals and provide utilisable magnesium oxide and silica. Different artificial magnesium rich silicates, for example slags of iron production, are possible raw materials as well. The magnesium content of the materials should be at least 10 %, preferably above 30%. The magnesium to silica ratio of natural magnesium silicates can vary widely: e.g. possible Mg:Si ratio of: Serpentine ~1.5 [e.g. Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]; Chlorite-group Minerals [e.g. Mg-clinochlor (Mg,Fe<sup>2+</sup>)<sub>5</sub>Al[(OH)<sub>8</sub>AlSi<sub>3</sub>O<sub>10</sub>]; Talc - 0.75 [e.g. Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>], forsterite -0.5 [e.g. Mg<sub>2</sub>SiO<sub>4</sub>] and enstatit -0.33 [e.g. MgSiO<sub>3</sub>].

**[0014]** The third component is a substance comprising magnesium carbonate either hydrated or un-hydrated and optionally magnesium hydroxide and designated hydrated magnesium carbonate. It corresponds to the empirical sum formula :



wherein  $x \geq 1$  and  $y$  and/or  $z \geq 0$  and  $x, y, z$  may be integers but do not have to and the carbonate can be non-stoichiometric. One preferred hydrated magnesium carbonate is hydromagnesite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> · 4H<sub>2</sub>O]. These substances are either found naturally or are produced synthetically, as for example synthetic forms like hydromagnesite, basic magnesium carbonate, magnesia alba and/or varieties of the listed compounds produced through precipitation. In view of the hardening time a hydrated magnesium carbonate with not too much Mg(OH)<sub>2</sub> is preferred [Mg(OH)<sub>2</sub> < 10%]. The BET surface of precipitated hydrated magnesium carbonate is usually more than 5 m<sup>2</sup>/g whereby samples with a BET surface - 10 m<sup>2</sup>/g are designated heavy and those with a surface  $\geq 20$  m<sup>2</sup>/g are designated light. Particularly useful is hydrated magnesium carbonate with a surface of around 21 m<sup>2</sup>/g, around 30 m<sup>2</sup>/g or around 40 m<sup>2</sup>/g. In terms of price, workability and performance mixtures of different hydrated magnesium carbonates were possible, e.g. 60 % heavy and 40 % light or 60 % heavy and 30 % with a surface - 20 m<sup>2</sup>/g and 10 % of material with a surface - 40 m<sup>2</sup>/g.

**[0015]** The binder composition according to the invention preferably contains the magnesium oxide and the hydrated magnesium carbonate in a weight ratio in the range of from 1:20 to 20:1, preferably from 1:10 to 10:1 and most preferably from 1:1.5 to 1.5:1. The weight ratio of Mg (from MgO and hydrated magnesium carbonate):reactive Si can range from 10:1 to 1:10, preferably from 1:5 to 3:1, more preferably from 1:3 to 2:1 and most preferably from 1:1.5 to 1.5:1. The total amount of Si in the system can vary widely depending on the composition of the source of reactive silica. The other components could also contain Si. For the ratio of Mg to Si only the amount of reactive silica is taken into account, SiO<sub>2</sub> not available for hydration like e.g. from fillers or crystalline parts of a fly ash is ignored.

**[0016]** The amount of material used as source of reactive silica (e.g. diatomaceous earth, micro-silica, silica fume, fine to ultra-fine quartz powder, (calcined) siliceous earth, natural puzzolans, synthetic puzzolans, blast furnace slag, fly ash, burnt oil shale, sewage sludge ash, rice husk ash, glass powder, etc.) in the binder composition ranges typically from 15 to 99 % by weight of the binder composition, preferably from 20 to 80 % by weight, most preferably from 30 to 70 % by weight. In case of high proportions of reactive silica in the material used like e.g. for micro silica or silica fume, the amount of the material and the amount of reactive silica are essentially the same. For materials with lower proportions of reactive silica the amount of source material is substantially higher than that of reactive silica.

**[0017]** The combined amount of magnesium oxide (including its impurities) and hydrated magnesium carbonate typically ranges from 1 to 85 % by weight of the composition, preferably from 5 to 50 % and most preferably from 10 to 40 %.

**[0018]** The binder can consist of magnesium oxide, hydrated magnesium carbonate and silica, but typically it contains one or more usual additive(s). Naturally, the amounts of all components of one composition have to add up to 100 %.

**[0019]** As usual, the binder according to the invention may contain additives like various salts, e.g. carbonates and

hydroxides, water glass [ $M_2O \cdot n SiO_2$ ; normally  $M = Na$  and / or  $K$  and  $n$  between 1 to 4] etc. to adjust its properties. Additives are used in their usual amounts and can be added as powder through mixing or intergrinding or as solution (e.g. waterglass,  $Na_2CO_3$ ,  $K_2CO_3$ , etc.).

**[0020]** Minor components, for example soluble carbonates, calcium hydroxide [ $Ca(OH)_2$ ], free lime, calcined dolomite / magnesium rich calcite, sources of aluminium and / or iron etc., can be added. Preferably, the amount of extra calcium compounds, e.g.  $Ca(OH)_2$  and/or  $CaO$ , has to be limited, as calcium ions form calcite in the presence of hydromagnesite which results in a decrease of its efficacy.

**[0021]** One preferred additive are plasticizers. Especially preferred are polyacrylate and polycarboxylate ether based superplasticizers, lignosulfonates, sulfonated naphthalene and/or melamine formaldehydes. Mixtures can be used. Preferably the binder contains from 0.05 to 5 % by weight of the composition of one or more plasticizer(s), more preferably from 0.5 to 3 % by weight and most preferred from 1 to 2 % by weight.

**[0022]** A further preferred additive are accelerators, especially such that additionally enhance the reactivity of the components of the binder. Preferred are  $NaHCO_3$ ,  $Na_2CO_3$  with or without water of crystallization,  $K_2CO_3$  with or without water of crystallization, free lime, portlandite, calcined dolomite (preferably low temperature calcined, i.e. at up to 750 °C), water glass, etc. and mixtures of thereof. Preferred amounts of the accelerators are 0.01 % to 25 % by weight of the binder composition, preferably 0.1 % to 5 % by weight. Also applicable are  $NaCl$ ,  $CaCl$  with or without water of crystallization, sources of sulphate, phosphate or chlorides and mixtures thereof and with the preferred accelerators but only in very small dosages, typically in the range of 0.01% to 2%, to avoid the formation of water soluble sored phases.

**[0023]** In one embodiment water soluble carbonates and/or hydrogencarbonates are used as accelerator. Sodium hydrogencarbonate was found to provide an exceptional increase in early strength and reduction of delay until stiffening. Carbonates can be useful when steel reinforcement is present due to the increase in pH.

**[0024]** The water to binder ratio is preferably from 0.15 to 1.50, more preferred from 0.3 to 0.75. It is adapted to the intended use, e.g. a lower ratio is selected for high ultimate strength and a higher ratio in case of use for a floor screed.

**[0025]** In a preferred embodiment the binder composition substantially excludes constituents that lead to the formation of unwanted phases like sored cement, such as chlorides, sulfates, phosphates etc. or includes only small amounts thereof so that the formation of the unwanted phases is negligible.

**[0026]** A preferred binder composition includes [1] fresh calcined and/or aged magnesium oxide [BET normally  $\geq 10 m^2/g$ ], [2] a source of reactive  $SiO_2$  (Blaine surface  $\geq 2000 cm^2/g$ : ground diatomaceous earth; micro-silica, silica fume, fine to ultra-fine quartz powder, (calcined) siliceous earth, natural and/or synthetic puzzolans: blast furnace slag, fly ash, burned oil shale, Sewerage sludge ash, rice husk, glass powder, etc.), [3] hydromagnesite (BET normally  $\geq 10 m^2/g$ ), [4] plasticizer and [5] minor solidification-accelerating additive: soluble carbonates [for example  $NaHCO_3$ ,  $Na_2CO_3$ , etc.]; free lime and/or portlandite and/or subsidiary at low temperature calcined dolomite [ $\leq 750^\circ C$ ] and/or possibly a source of chloride, sulphate, phosphate, water glass, puzzolane etc.

**[0027]** The workability of a binder-water system can be improved by the addition of plasticizers, such as lignosulfonates, sulfonated naphthalene, sulfonated melamine formaldehydes, polyacrylate and polycarboxylate ether based superplasticizers. Superplasticizers are particularly used to lower the water content of the composition in order to obtain a denser microstructure and thus a product with higher strength and better durability. A low addition of water will generally result in a higher viscosity of the composition which is difficult to work with. However, the application of a superplasticizer enables the water-binder system to retain good workability and eases its use and placement. The dosage of superplasticizers is advantageously adapted to the used source of reactive  $SiO_2$ . If, e.g. diatomaceous earth is used as a  $SiO_2$  source, no negative effect, concerning a possible retardation or a decrease of the final strength, is observed utilizing dosages from 0.05 % to 5 %, preferably 0.5 % to 3 % and most preferably 1 % to 2 % of polycarboxylate type superplasticizer (dry powder). However, additions above 0.3 % of polycarboxylate type superplasticizer in mixtures with blast furnace slag resulted in a slight decrease of the early age compressive strength.

**[0028]** The main components of the binder are preferably mixed very well (due to their high fineness) to achieve a homogenous composition. Mixing can be performed with any known devices. In one embodiment the component powders are dry mixed and homogenized in a Taumel-mixer. Liquid additives, i.e. liquid substances or such typically provided as solution like the polycarboxylate type superplasticizer are preferably added to the mixing water.

**[0029]** The binder can be used to formulate a concrete, mortar or plaster and other construction chemical products. It replaces the known binders portland cement, high alumina cement and the like in these materials. To this end the common further constituents are mixed in a manner known per se with the binder according to the invention. It is within the scope of the invention to provide a dry mix containing a part of the binder as well as all or a part of the additives and other constituents if wanted and to add the rest of the binder constituents as well as eventually remaining other additives and constituents at the site of use, e.g. prior to or concurrently with the water.

**[0030]** The binder according to the invention can be advantageously used for massive construction, precast building elements, repair grouts, tile adhesives, underground and mining applications, fixation of contaminants, top layer repair and protective applications.

**[0031]** Besides water, aggregate is typically added to the binder. Sand, natural gravel and crushed stone are mainly

used for this purpose. Recycled aggregates (from construction, demolition and excavation waste) are increasingly used as partial replacements of natural aggregates, while a number of manufactured aggregates are also permitted. The amount of aggregate usually ranges from 25 to 70 % by weight of the building material and can be up to 95 % by weight. The size depends on the intended application.

**[0032]** The binder has depending on its composition (w/b ratio, used aggregate, used source of SiO<sub>2</sub>, form of the product body) a white to light grey colour, which is retained after the material is hydrated. This feature as well as the light weight of the produced components allows the binder composition to be used for premium construction products. The addition of different pigments is possible. The product can be optimized by addition of filler: for example limestone, glass granulates, etc.

**[0033]** The binder composition offers the possibility to incorporate/bind heavy metals which are more soluble at high pH-values. First test trials with addition of heavy metals like Zn and Pb (as oxides or carbonates) in the range from 1 to 5 % to mixtures of MgO, SiO<sub>2</sub> and hydromagnesite showed that they have no negative effect on the hardening.

**[0034]** An additional and surprising benefit is the availability of CO<sub>2</sub> through the reaction of hydromagnesite with water. In contact with water and a suitable chemical species to bind carbonate ions, it seems that the hydromagnesite releases its carbonate into the solution. If for example calcium is available the available free CO<sub>2</sub> can bind Ca<sup>2+</sup> ions and precipitates the Ca<sup>2+</sup> ions as calcite.

**[0035]** The invention will be illustrated further with reference to the examples that follow, without restricting the scope to the specific embodiments described. If not otherwise specified any amount in % or parts is by weight and in the case of doubt referring to the total weight of the composition/mixture concerned.

**[0036]** The invention further includes all combinations of described and especially of preferred features that do not exclude each other. A characterization as "approximately", "around" and similar expression in relation to a numerical value means that up to 10 % higher and lower values are included, preferably up to 5 % higher and lower values, and in any case at least up to 1 % higher and lower values, the exact value being the most preferred value or limit.

#### Example 1

**[0037]** The reaction of several combinations of the substances with water was tested. A combination of brucite [Mg(OH)<sub>2</sub>] or magnesite [MgCO<sub>3</sub>] or hydromagnesite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O] with SiO<sub>2</sub>, either ground diatomaceous earth, silica fume, or calcined siliceous earth, and H<sub>2</sub>O, does not show any or only very low hardening effect within 7 days. The combination of at least two of brucite [Mg(OH)<sub>2</sub>], magnesite [MgCO<sub>3</sub>] and hydromagnesite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O] with a source of reactive SiO<sub>2</sub> and H<sub>2</sub>O did also not show any or only very low hardening effect within 7 days. Mixing MgO and SiO<sub>2</sub> with water reveals a measurable stiffness after 1 to 2 days, depending on the reactivity of the MgO. This is probably due to precipitation of Mg(OH)<sub>2</sub> and further increased due to the formation of a magnesium carbonate (see formula above) and MSH phases. A significant hardness is reached after 28 days. The combination of MgO and hydromagnesite leads to a hardened product upon contact with water as a result of the formation of brucite and different magnesium carbonates. Mixtures of MgO, hydromagnesite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O], and SiO<sub>2</sub>, optionally with other minor components, revealed superior results in comparison to every other composition. Also, the addition of a more reactive source of SiO<sub>2</sub> lead to an increase of the compressive strength. First trials used ground diatomaceous earth [-30 % amorphous SiO<sub>2</sub>] and a second trial used calcined siliceous earth [-87 % reactive quartz, ~10 % amorphous SiO<sub>2</sub>].

#### Example 2

**[0038]** The development of compressive strength and the crystal structure were determined for the following compositions:

M1: 50% MgO / 45% SiO<sub>2</sub> (ground diatomaceous earth) / 5% NaHCO<sub>3</sub>

M2: 25% MgO / 25% Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O / 45% SiO<sub>2</sub> (ground diatomaceous earth) / 5% NaHCO<sub>3</sub>

M3: 25% MgO / 25% Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O / 50% SiO<sub>2</sub> (calcined siliceous earth)

M4: blast furnace slag

M5: 2.5 % MgO / 5 % Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O / 92.5 % blast furnace slag

The water/binder ratio for M1, M2, and M3 was 0.75 and 1% PCE (polycarboxylat plasticizer) with regard to the dry mix was added on top. The water/binder ratio for M4 and M5 was 0.35 and 0.1% PCE with regard to the dry mix was added on top. For M1 and M2 corundum was used as internal standard. The ground blast furnace slag was composed of 37.8 % CaO, 33.4 % SiO<sub>2</sub>, 14.3 % Al<sub>2</sub>O<sub>3</sub>, 9.3 % MgO (RFA) and had a Blaine fineness of -4070 cm<sup>2</sup>/g. The samples were produced by mixing the binder composition with water at room temperature, filling the slurry in different moulds (for example: 40 mm x 40 mm x 1600 mm) and curing inside the mould for 24 hours at 20°C and at 95 percent relative humidity. After 24h the samples were demoulded and cured for 7 days below water or in air in an air-conditioned room.

[0039] According to X-ray diffraction measurements the initial reaction product of M2 after 1 day of hydration was a surprisingly low amount of brucite and a significant amount of X-ray amorphous phase which seems to be MSH, maybe mixture of X-ray amorphous carbonate and MSH. After 7 or 28 days respectively, the amount of brucite decreased significantly whereas the amount of X-ray amorphous phase further increased. The compressive strength of the samples increased as well. The mixtures of 25% MgO + 25% hydromagnesite + 50% reactive SiO<sub>2</sub> had a higher compressive strength than mixtures of 50% MgO + 50% reactive SiO<sub>2</sub> (same preparation and w/b ratios). The variation of the SiO<sub>2</sub> source lead to an additional increase of the early and final strength. The results show that the hardening mechanism of the binder according to the present invention is a formation of magnesium silicate hydrate and acceleration of its formation through addition of the special magnesium carbonate.

[0040]

Table 1

	Brucite [%]			X-Ray amorphous content [%]			Compr. Strength [MPa]		
	1d	7d	28d	1d	7d	28d	1d	7d	28d
M1	38	35.8	37.1	31.7	30.3	29.5	0	10.3	10.2
M2	18	12.9	6.8	33.8	37.4	43.8	0	15.1	17.3
M3							18.3	22.7	33.5
M4							0	2.8	10.9
M5							20.7	23.9	36.65

[0041] The results of a heat of hydration measurement (determined by a differential scanning calorimeter [TAM-air]) of the paste of samples M1, M2 and M3 with a w/b of 0.75 are depicted in figure 1 and 2 and table 2.

[0042]

Table 2

		Unit	M1	M2	M3
			20.-27.10.10	20.-27.10.10	22.-29.11.10
w/z	Value		0.75	0.75	0.75
0-2	Hours	J/g	20	17	49
0-6	Hours	J/g	254	106	189
0-8	Hours	J/g	311	157	196
0-12	Hours	J/g	347	179	197
0-24	Hours	J/g	363	187	198
0-2	Days	J/g	376	199	201
0-3	Days	J/g	386	211	203
0-4	Days	J/g	395	223	206
0-5	Days	J/g	403	232	208
0-6	Days	J/g	409	236	212
0-7	Days	J/g	415	239	215

[0043] A dependence of the position of the peak and its shift depending on the used source of silica can be clearly seen during the first 8 hours of hydration. The addition of a highly reactive source of SiO<sub>2</sub> shifted the peak to earlier times which directly results in a significant higher 1 day compressive strength. In table 2 the cumulative specific heat Q of the specific intervall up to seven days of hydration is given and in figure 2 the measured data given in table 2 is plotted over time. The measurements reveal that the cumulative specific heat Q continues to grow at a slow rate after one day of hydration.

## Claims

- 5  
1. Binder composition forming magnesium silicate hydrate upon reaction with water comprising magnesium oxide, a reactive  $\text{SiO}_2$  and a hydrated magnesium carbonate of formula  $x \text{MgCO}_3 \cdot y \text{Mg(OH)}_2 \cdot z \text{H}_2\text{O}$ , wherein  $x \geq 1$ , the carbonate may be non-stoichiometric and at least one of  $y$  or  $z \geq 0$  and  $x, y, z$  may be integers or rational numbers, wherein the weight ratio of magnesia to hydrated magnesium carbonate ranges from 1:20 to 20:1 and wherein the weight ratio of Mg (from the Magnesium oxide and the hydrated magnesium carbonate) to reactive Si ranges from 1:10 to 10:1.
- 10  
2. Binder composition as claimed in claim 1, **characterized in that** the weight ratio of magnesia to hydrated magnesium carbonate ranges from 1:10 to 10:1 and preferably from 1:1,5 to 1,5:1.
- 15  
3. Binder composition as claimed in claim 1 or 2, **characterized in that** the binder composition comprises a source of the reactive  $\text{SiO}_2$  selected from ground diatomaceous earth, micro-silica, silica fume, fine to ultra-fine quartz powder, (calcined) siliceous earth, natural and/or synthetic puzzolans, blast furnace slag, fly ash, burnt oil shale, sewage sludge ash, rice husk ash, glass powder and mixtures of two or more thereof.
- 20  
4. Binder composition as claimed in claim 1, 2 or 3, **characterized in that** a source of reactive  $\text{SiO}_2$  has a Blaine surface of  $\geq 2000 \text{ cm}^2/\text{g}$ , preferably from 2500 to 11000  $\text{cm}^2/\text{g}$ , most preferably from 3000 to 6000  $\text{cm}^2/\text{g}$ .
- 25  
5. Binder composition as claimed in at least one of claims 1 to 4, **characterized in that** the amount of a material used as source of reactive silica in the binder composition ranges from 15 to 98 % by weight of the binder composition, preferably from 20 to 80 % by weight, most preferably from 30 to 70 % by weight.
- 30  
6. Binder composition as claimed in at least one of claims 1 to 5, **characterized in that** the combined amount of magnesium oxide and hydrated magnesium carbonate in the binder composition ranges from 2 to 85 % by weight of the composition, preferably from 10 to 50 % by weight and most preferably from 20 to 40 % by weight.
- 35  
7. Binder composition as claimed in at least one of claims 1 to 5, **characterized in that** one or more plasticizers are contained.
- 40  
8. Binder composition as claimed in claim 7, **characterized in that** the one or more plasticizers are selected from polyacrylate and polycarboxylate ether based superplasticizers, lignosulfonates, sulfonated naphthalene and/or melamine formaldehydes.
- 45  
9. Binder composition as claimed in claim 7 or 8, **characterized in that** the plasticizer is present in an amount of from 0.05 % to 5 % by weight of the composition, preferably from 0.5 % to 3 % and most preferably from 1 % to 2%.
- 50  
10. Binder composition as claimed in at least one of claims 1 to 9, **characterized by** comprising 0.01 % to 25 % by weight of the composition, preferably 0.1 % to 5 % of one or more of  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , free lime, portlandite, calcined dolomite, and water glass.
- 55  
11. Building material made from the binder composition according to anyone of claims 1 to 10 by mixing with water at a water to binder ratio of 0.15 to 1,50.
12. Building material according to claim 11, **characterized in that** it contains up to 95 % by weight, preferably 25 to 70 %, of aggregates and or filler.
13. Use of a binder composition as claimed in anyone of claims 1 to 10 for massive construction, precast applications, repair grouts, tile adhesives, underground and mining applications, fixation of contaminants, especially heavy metal ions, top layer repair and protective applications.

Fig. 1: TAM-air measurements; continuous line – M1; dots and dashes – M2 and dashes – M3

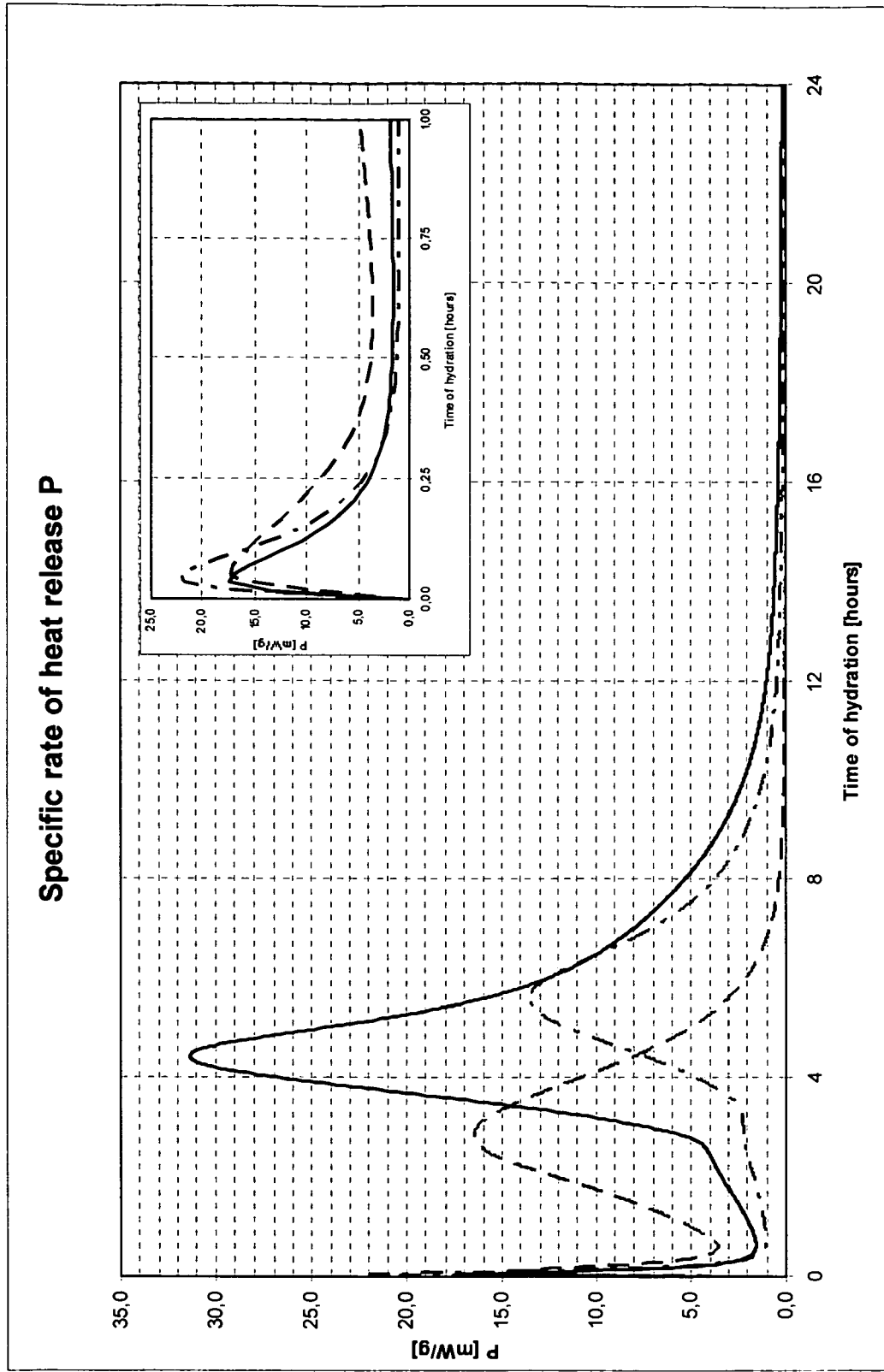
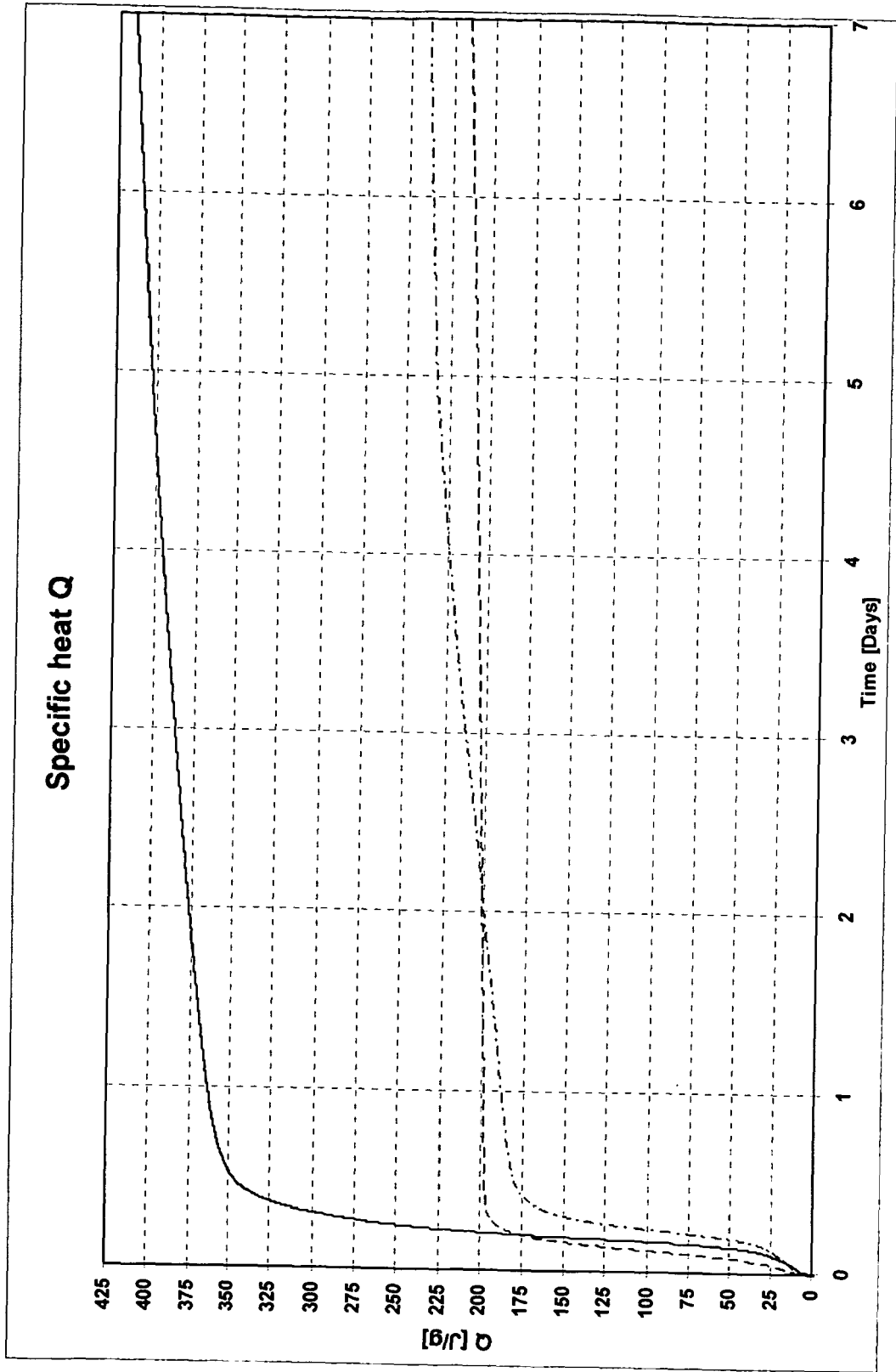


Fig. 2: TAM-air measurements; continuous line – M1; dots and dashes – M2 and dashes – M3





## EUROPEAN SEARCH REPORT

Application Number  
EP 11 00 2869

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2009/156740 A1 (NOVACEM LTD; VLASOPOULOS NIKOLAOS [GB]; CHEESEMAN CHRISTOPHER ROBERT []) 30 December 2009 (2009-12-30) * abstract * * page 16, paragraph 4 * * examples 3,5 * -----	1-13	INV. C04B28/10 C04B28/18
A	RU 2 233 255 C1 (POTSELUEVA, GONCHAROV) 27 July 2004 (2004-07-27) * abstract * -----	1-13	
A	S. BANERJEE: "Utilization of Fly Ash in Construction by Improved Chemical Bonding", THIRD CONFERENCE ON UNBURNED CARBON ON UTILITY FLY ASH, 1997: NATIONAL ENERGY TECHNOLOGY LABORATORY; 1997., 1997, XP000002657337, * page 2, paragraph 2 * -----	1-13	
A	CHEMICAL ABSTRACTS, November 1982 (1982-11), XP000184104, ISSN: 0009-2258 * abstract * -----	1-13	TECHNICAL FIELDS SEARCHED (IPC) C04B
A	BJORN MYHRE, ELKEM MATERIALS: "Cement-free Castables in the System MgO-SiO <sub>2</sub> : The effect of bond phase modifiers on strength", AMERICAN CERAMIC SOCIETY, 93RD ANNUAL MEETING CINCINNATI, OHIO, 2 May 1991 (1991-05-02), XP000002657338, * table 1 * -----	1-13	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 12 September 2011	Examiner Roesky, Rainer
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

1  
EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 11 00 2869

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-09-2011

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009156740 A1	30-12-2009	AU 2009263979 A1	30-12-2009
		CA 2727072 A1	30-12-2009
		CN 102083764 A	01-06-2011
		EP 2297062 A1	23-03-2011
		KR 20110053926 A	24-05-2011
-----			
RU 2233255 C1	27-07-2004	NONE	
-----			

EPO FORM P0489

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- WO 2009156740 A [0003]